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Hole Transport in Triphenylmethane Doped Polymers

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Hole mobilities have been measured in poly(styrene) (PS) doped with a series of triphenylmethane (TPM) derivatives with different dipole moments. The results are described by a formalism based on disorder, due to Bässler and coworkers. The formalism is premised on the assumption that charge transport occurs by hopping through a manifold of localized states that are distributed in energy. A key parameter of the formalism is the energy width of the hopping site manifold. For TPM doped PS, the widths are between 0.106 and 0.117 eV, increasing with increasing dipole moment. The widths are described by a model based on dipolar disorder. The model is based on the assumption that the total width is comprised of a dipolar component and a van der Waals component. For TPM doped PS, the dipolar components are between 0.021 and 0.052 eV, while the van der Waals components are 0.105 eV. The van der Waals components are significantly larger than for PS doped with a wide range of triarylamine (TAA) molecules. The difference in the van der Waals component is described by a charge delocalization argument and is the principal reason for the difference in mobility of TPM and TAA doped polymers.

KEYWORDS: disorder controlled hopping, hole transport, triphenylmethane doped polymers

1. Introduction

Molecularly doped polymers contain a strong electron donor or acceptor in a polymer host. Hole or electron transport occurs by charge transfer between adjacent donor or acceptor molecules, respectively. This can be described as a one-electron oxidation-reduction or donor-acceptor process between neutral molecules and their charged derivatives.¹⁻⁴⁾ Mobilities of these materials are very low, strongly field and temperature-dependent, as well as dependent on the dopant molecule, dopant concentration, and the host polymer.

Many recent studies have been described by a formalism based on disorder, due to Bässler and colleagues.⁵⁻⁹⁾ The formalism is based on the assumption that charge transport occurs by hopping through a manifold of localized states with superimposed energetic (diagonal) and positional (off-diagonal) disorder. A key parameter of the formalism is the variance of the hopping site energies, or DOS (density-of-states). The formalism envisages the energy of the charge carrier at each hopping site as randomized with a Gaussian distribution, characterized by an energy width σ of about 0.1 eV, determined by the local environment of the hopping site. A more detailed discussion of the predictions and assumptions of the formalism has been given in the preceding paper.

There is considerable evidence that σ is related to the dipole moment of the donor or acceptor molecule and the polymer repeat unit. This was first demonstrated by Sugiuchi *et al.*¹⁰⁾ who reported that hole mobilities of a series of donor molecules doped into a polycarbonate decreased in a near exponential manner with the dipole moment of the donor molecule. The role of the dopant molecule was later described in more detail by Borsenberger *et al.*,¹¹⁻¹⁴⁾ Borsenberger and Gruenbaum,¹⁵⁾ Borsenberger and Heun,¹⁶⁾ Borsenberger and O'Regan,¹⁷⁾ Young and Fitzgerald,¹⁸⁾ and Young *et al.*¹⁹⁾ A similar effect, related to the host polymer, can be inferred from the work of Takeshita *et al.*,²⁰⁾ Sasaki *et al.*,²¹⁾ Borsenberger,²²⁾ Kanemitsu and Einami,²³⁾ Yuh

and Pai,²⁴⁻²⁷⁾ Borsenberger and Bässler,²⁸⁾ Borsenberger and Rossi,²⁹⁾ and Kanemitsu.³⁰⁾ A review of dipolar effects on transport phenomena in doped polymers has recently been given by Young *et al.*¹⁹⁾ The phenomena have been described by an argument based on dipolar disorder, due to Borsenberger and Bässler,³¹⁾ and in a more quantitative manner by the later work of Dieckmann *et al.*³²⁾ Sugiuchi and Nishizawa,³³⁾ Young,³⁴⁾ and Richert and Loring.³⁵⁾ The argument is that a random distribution of permanent dipoles generates fluctuations in electrostatic potential that add to local variations of potential resulting from van der Waals forces. Adding dipoles randomly increases the fluctuations of hopping site energies a carrier experiences. The result is that the total width of the DOS is determined by a dipolar component and a van der Waals component. Predictions of the argument agree with results reported for a wide range of triarylamine (TAA) doped polymers.^{12,14,16,17)} The results can be described by the model of Young and have led to the conclusion that the van der Waals component increases with increasing molecular dilution. This effect, which is not predicted from first order arguments, has been attributed to an increase in structural randomness with dilution.

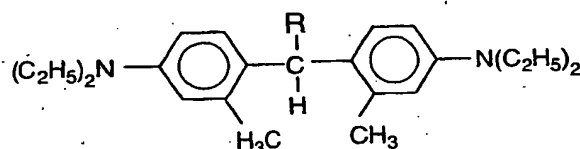
In an early study³⁶⁾ of the triphenylmethane (TPM) derivative, bis(4-N,N-diethylamino-2-methylphenyl)-4-methylphenylmethane, doped into poly(styrene) (PS), the width of the DOS was reported as significantly larger than for TAA-doped PS with comparable dipole moments. Similar effects were later observed in a series of vapor-deposited TPM glasses, as described in the preceding paper. This observation has been rationalized by the argument that relative to the TAA molecules, the TPM molecules have a larger van der Waals component. This was explained by a charge delocalization argument. The argument is based on the assumption that the van der Waals contribution is due to a charge-induced dipolar interaction and leads to the conclusion that the van der Waals component increases as the molecule becomes less conjugated.

To better understand the role of the van der Waals interactions, it is of interest to extend the preceding study of vapor-deposited TPM glasses to doped polymers. This study describes the results of an investigation of hole transport in a series of TPM derivatives doped into PS. The dipole moments of the derivatives are between 1.33 and 3.20 D. PS was selected as the polymer because the dipole moment of the repeat unit is near-zero, thus the polarity of the polymer can be neglected. To our knowledge, there have been only three studies of TPM-doped polymers described in the literature: Pai *et al.*,³⁾ Abkowitz *et al.*,³⁷⁾ and Borsenberger.³⁶⁾ The emphasis of this study, however, concerns the dipole moments of the TPM molecules which was not addressed in the earlier studies.

2. Experimental

The derivatives investigated are bis(4-N,N-diethylamino-2-methylphenyl) (4-methylphenyl)methane (TPM-A), bis (4-N,N-diethylamino-2-methylphenyl) 4-propylphenyl methane (TPM-B), bis (4-N,N-diethylamino-2-methylphenyl) (4-phenylphenyl) methane (TPM-C), bis (4-N,N-diethylamino-2-methylphenyl) (phenylmethane) (TPM-D), bis (4-N,N-diethylamino-2-methylphenyl) (4-methoxyphenyl) methane (TPM-E), and bis(4-N,N-diethylamino-2-methylphenyl) (4-chlorophenyl)methane (TPM-F). The molecular structures are illustrated in Fig. 1. In ref. 36, TPM-A is described as MPMP. The techniques used for the synthesis of the TPM derivatives have been summarized in the preceding paper. TPM-D was not included in the preceding study of molecular glasses, because amorphous layers of TPM-D cannot be prepared by vapor deposition techniques.

Samples were prepared by dissolving the appropriate ratios of TPM and PS in dichloromethane, then coating the solutions on Ni-coated polyethylene terephthalate substrates that had previously been coated with an 0.20 μm layer of N,N'-bis(2-phenethyl)-perylene-3,4:



Molecule	R
TPM - A	Ph-CH ₃
TPM - B	Ph-nC ₃ H ₇
TPM - C	Ph-Ph
TPM - D	Ph-H
TPM - E	Ph-OCH ₃
TPM - F	Ph-Cl

Fig. 1. Molecular structures of the TPM derivatives.

Table I. TPM doped PS properties.

Molecule	R ^{a)}	μ (D)	T_g (K) ^{b)}
TPM-A	Ph-CH ₃	1.3	335
TPM-B	Ph-nC ₃ H ₇	1.5	329
TPM-C	Ph-Ph	1.7	351
TPM-D	Ph-H	1.8	331
TPM-E	Ph-OCH ₃	2.1	338
TPM-F	Ph-Cl	3.2	338

^{a)}The phenyl substituents were in the para position.

^{b)}The TPM concentrations were 35% (by weight).

9,10-bis(dicarboximide) (PECI). The TPM concentrations were 35.0% (by weight). The PS was obtained from Sinclair-Koppers as Dylene 8X. The solids concentration of the coating solutions was 10%. To reduce the residual dichloromethane concentration, the samples were heated to 332 K for 2 h. From cross-section photomicrographs and capacitance measurements, thicknesses of the doped polymer layers were between 14.0 and 16.0 μm . Finally, a 0.03 μm Au layer was vapor deposited on the doped polymer free surface. During the deposition process, the samples were attached to a liquid N₂-cooled Cu block. Table I summarizes some of the relevant properties of the doped polymer layers.

The mobility measurements were by conventional time-of-flight techniques that have recently been reviewed by Melnyk and Pai.³⁸⁾ The techniques used in this study have been summarized in the preceding paper. The range of temperatures for which these measurements could be made was determined by the glass transition at high temperatures and signal-to-noise limitations at low temperatures. The field range was determined by dielectric breakdown at high fields and signal-to-noise problems at low fields. Over the range of fields and temperatures investigated, the transients were reversible with no indications of hysteresis.

3. Results

The temporal features of the photocurrent transients for TPM-doped PS agree with transients observed in most doped polymers: (1) an initial spike of very short duration, (2) a plateau of variable length, and (3) a long tail. Plateaus were observed for all fields and temperatures. The width of the tail is described by the tail broadening parameter W , defined³⁹⁾ as $W = (t_{1/2} - t_0)/t_{1/2}$, where $t_{1/2}$ is the time required for the photocurrent to decay to 1/2 its value at t_0 . Values of W are weakly field and temperature dependent, increasing with increasing field and decreasing temperature. At 296 K and 10⁵ V/cm, values are in the range of 0.49 to 0.51, nearly the same for all dopant molecules. Mobilities determined from transit times defined as $t_{1/2}$, or the method described by Scott *et al.*,⁴⁰⁾ gave essentially the same field and temperature dependencies.

Figure 2 shows the field dependencies of the mobility, plotted semilogarithmically versus $E^{1/2}$, for TPM-C-doped PS. The results can be described as $\mu \propto \exp(\beta E^{1/2})$, where β is a constant that decreases with increasing temperature. Values of β are between 2 and

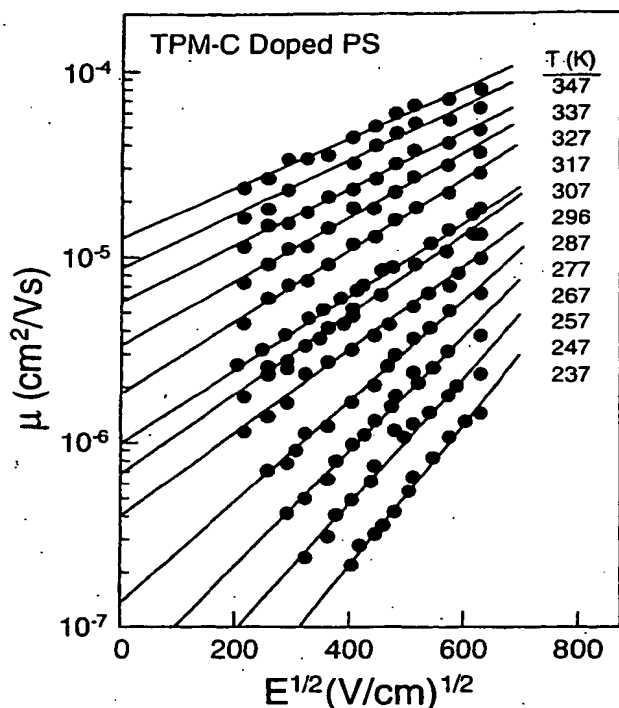


Fig. 2. Field dependencies of the mobility, parametric in temperature, for TPM-C doped PS.

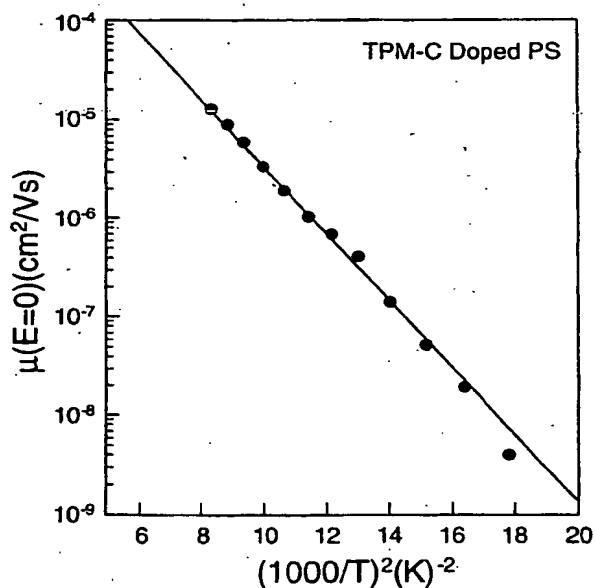


Fig. 3. Temperature dependence of the zero-field mobility for TPM-C doped PS. The zero-field values were derived by the extrapolation of the data in Fig. 2 to $E = 0$. The correlation coefficient of the solid line is 0.999.

$10 \times 10^{-3} \text{ (cm/V)}^{1/2}$.

According to the disorder formalism, σ and μ_0 can be determined from the slope and intercept of a semilogarithmic plot of the zero-field mobility versus T^{-2} . Figure 3 shows the results for TPM-C-doped PS. The results yield $\sigma = 0.110 \text{ eV}$ and $\mu_0 = 8.15 \times 10^{-3} \text{ cm}^2/\text{Vs}$.

The positional disorder parameter Σ can be deter-

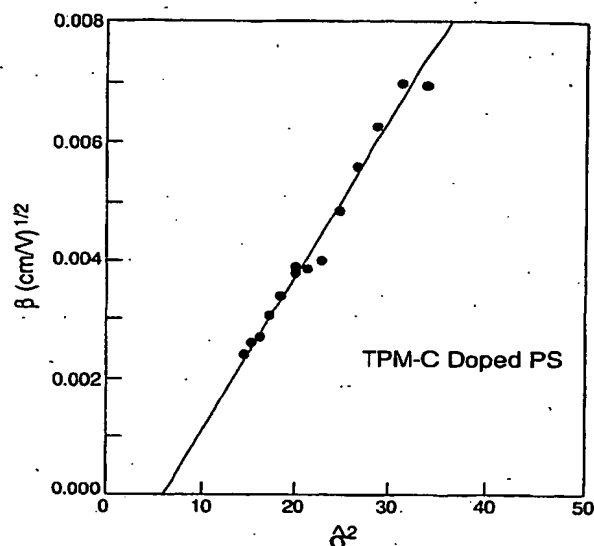


Fig. 4. β versus σ^2 for TPM-C doped PS. Here, $\beta = \partial \ln \mu / \partial E^{1/2}$ and $\sigma = \sigma/kT$. A value of 0.110 eV was used for σ , as derived from the data in Fig. 3. The correlation coefficient of the solid line is 0.973.

Table II. TPM doped PS transport properties.

Molecule	σ (eV)	Σ	μ_0 (cm²/Vs)	C (cm/V)¹/²
TPM-A	0.106	2.4	8.64×10^{-3}	2.6×10^{-4}
TPM-B	0.108	3.0	1.52×10^{-2}	2.6×10^{-4}
TPM-C	0.110	2.4	8.15×10^{-3}	2.6×10^{-4}
TPM-D	0.110	2.4	1.21×10^{-2}	2.4×10^{-4}
TPM-E	0.111	2.8	1.30×10^{-2}	2.6×10^{-4}
TPM-F	0.117	2.1	5.55×10^{-3}	2.8×10^{-4}

mined from the temperature dependence of the field dependencies of the mobility. The formalism predicts that β (the high field slopes in Fig. 2) versus σ^2 should be linear with a slope of $2.9 \times 10^{-4} \text{ (cm/V)}^{1/2}$. Here, $\sigma = \sigma/kT$. Σ can then be determined from the $\beta = 0$ intercept from the condition $\sigma = \Sigma^2$. Figure 4 shows the results for TPM-C-doped PS. As predicted, a linear relationship is observed. The slope is $2.6 \times 10^{-4} \text{ (cm/V)}^{1/2}$, in good agreement with values obtained by simulations. From the $\beta = 0$ intercept, $\Sigma = 2.4$.

In a similar manner, σ , μ_0 , Σ , and C were determined for TPM-A, TPM-B, TPM-D, TPM-E, and TPM-F-doped PS. The results are summarized in Table II. The results are in good agreement with earlier work on TPM-doped polymers by Pai *et al.*,³¹ Abkowitz *et al.*,³⁷ and Borsenberger.³⁶

4. Discussion

The key result of this study is that the width of the DOS increases with increasing dipole moment of the TPM molecules. Increasing the dipole moment from 1.33 to 3.20 D results in an increase in σ from 0.106 to 0.117 eV . These results are in accord with results obtained with vapor deposited TPM glasses.

The total width σ is determined by a dipolar compo-

nent σ_d and a van der Waals component σ_{vdw} . Assuming both can be described by Gaussian statistics

$$\sigma = (\sigma_{vdw}^2 + \sigma_d^2)^{1/2} \quad (1)$$

Young³⁴⁾ has described the dipolar component as

$$\sigma_d = \frac{7.04c^{1/2}p}{\rho^2\epsilon} \quad (2)$$

where c is the fraction of lattice sites occupied by dipoles, p the dipole moment (in D), ρ the intersite distance (in Å), ϵ the dielectric constant, and σ_d is in eV. Equations (1) and (2), in conjunction with the results in Table II, provide a means for evaluating σ_d and σ_{vdw} . Substituting $c = 0.35$, $\epsilon = 3.0$, and the appropriate values of ρ and p into eq. (2) yields the results summarized in Table III. The results show $\sigma_{vdw} \sim 0.105$ eV, independent of the TPM dipole moment. This provides further justification for separating the total width into a component that is dependent on the dipole moment, and a component that is not.

It is of interest to compare σ_{vdw} for TPM and TAA-doped polymers. Values of σ_{vdw} have been reported for tri-*p*-tolylamine,¹⁴⁾ 1,1-bis(di-4-tolylaminophenyl) cyclohexane,⁴¹⁾ N,N'-bis(3-methylphenyl)(1,1'-biphenyl)-4,4'-diamine,⁴¹⁾ and N,N',N'',N'''-tetrakis (4-methylphenyl)(1,1'-biphenyl)-4,4'-diamine.⁴¹⁾ In all cases, the host polymer was PS and the TAA concentration 35%. The values are 0.082, 0.081, 0.083, and 0.084 eV, respectively, considerably less than for TPM-doped polymers. The higher value of σ_{vdw} is the principal reason why mobilities of TPM-doped polymers are lower than for TAA-doped polymers. The prefactor mobility and the degree of positional disorder are essentially the same for both.

In the preceding paper, the difference was described by a conjugation, or charge delocalization argument. The argument is based on the fact that the TAA molecules are highly conjugated, while TPM derivatives are not. In doped polymers, the occupancy of a hopping site by an excess charge induces a displacement of the electronic clouds of the surrounding molecules. These displacements create a charge-induced dipolar cloud that surrounds the hopping site. It is the fluctuations of the dipolar cloud that are the physical origin of the van der Waals component. The fluctuations of the dipolar cloud are due to the fluctuations of molecular orientations of the hopping site molecule and the surrounding molecules. The key assumption of the charge delocalization argument is the fluctuations in molecular orientation are more significant for weakly conjugated molecules. For highly

conjugated molecules, fluctuations of orientation are less important, due to the fact that the charge distribution is more-or-less uniform over the molecular surface. To first order, the argument leads to the prediction that the van der Waals contribution increases with decreasing conjugation, which is consistent with the results observed for both TPM and TAA vapor-deposited glasses and doped polymers. Similar arguments have been proposed earlier by Yokoyama,⁴²⁾ Tanaka *et al.*,⁴³⁾ Aratani *et al.*,⁴⁴⁾ Kitamura and Yokoyama,^{45,46)} and Hirose *et al.*⁴⁷⁾ All are based on the assumption that the charge distribution on the dopant molecule plays an important role in the charge transfer process.

Finally, we comment briefly on the prefactor mobilities and the positional disorder. Values of μ_0 are similar for all TPM molecules and suggest that μ_0 is not influenced by the dipole moment of the dopant molecule. Values of Σ are also similar for all molecules and agree with literature results reported for a wide range of donor and acceptor doped polymers. These observations suggest that positional disorder is mainly determined by geometrical considerations, as one would intuitively suspect, and is relatively insensitive to molecular structure.

5. Summary and Conclusions

Hole mobilities have been measured in a series of TPM derivatives doped into PS. The results can be described by the disorder formalism and yield a width of the DOS that increases with increasing dipole moment of the TPM molecules. The width can be described by a model based on dipolar disorder. The model leads to the conclusion that the width is comprised of a dipolar component that increases with increasing dipole moment and a van der Waals component that is constant. The van der Waals component is significantly larger than for a wide range of TAA-doped polymers and is the principal reason for the difference in mobility between TPM and TAA-doped polymers.

The difference in the van der Waals component can be rationalized by an argument based on charge delocalization. The key assumption of the argument is that fluctuations in molecular orientation, and thus the charge-induced dipolar cloud which is the physical origin of the van der Waals component, are more significant for weakly conjugated molecules. For strongly conjugated molecules, fluctuations of molecular orientation are less important.

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Table III. Width of the DOS of TPM doped PS.

Molecule	Σ (eV)	σ_d (eV)	σ_{vdw} (eV)
TPM-A	0.106	0.021	0.104
TPM-B	0.108	0.025	0.105
TPM-C	0.110	0.027	0.106
TPM-D	0.110	0.029	0.106
TPM-E	0.111	0.034	0.104
TPM-F	0.117	0.052	0.105

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